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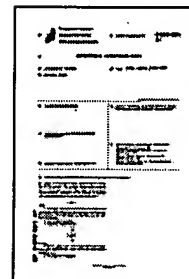
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? Abstract:
 

1. Thermoplastic moulding compositions stabilised against thermolytic degradation and having small residual monomer contents, based on acrylonitrile, styrene (or alpha-methylstyrene) and rubbers, characterised by a content of 0.01 to 10% by weight (based on the total weight) of compounds selected from alkyl mercaptan, araliphatic mercaptans, aromatic mercaptans, heterocyclic mercaptans, thiocarboxylic acids and addition products of episulphides with polyols, polyphenols or aliphatic amines, in each case having 1 to 18 C atoms per SH group.



High  
Resolution

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(54) An adhesive.

(57) Aqueous based adhesives having improved shear properties are prepared from acrylate type latices, styrene-butadiene type latices, or ethylene-vinyl acetate latices, which contain a carboxylic acid monomer, and have been neutralized to a pH equal to or greater than about 6, the neutralization comprising utilising an agent selected from hydroxides and salts of lithium, sodium, potassium, and a mixture thereof. The adhesives have improved shear properties.

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An adhesive

The present invention pertains to aqueous based adhesives having improved shear strength.

Due to rising costs and environmental concern there has been significant interest in developing adhesives which do not utilize hydrocarbon solvents. There are two options available to adhesive manufacturers who wish to minimize the use of hydrocarbon solvents. The manufacturer may use a hot melt adhesive or an aqueous based adhesive. Aqueous based adhesives are relatively simple to use and do not require extensive equipment modification over solvent based adhesive systems. Aqueous based adhesives have come under the criticism that they do not provide sufficient shear strength. There exists a need to develop aqueous based adhesives, and particularly pressure sensitive adhesives having improved shear strength.

It has been found that the shear strength of adhesives based on latexes containing functional groups such as carboxylic acid, amide, aldehyde and anhydrides of dicarboxylic acids, may be improved by the post polymerization neutralization of such latexes with a monovalent metal alkali. Without wishing to be bound by theory, it is believed that the size of the monovalent ion contributes to the shear strength developed and that the smaller the monovalent metal ion the higher the shear strength.

There is a significant body of art relating to the use of multi-valent metal ions, amines or diamines to cross link polymers. Such methods are disclosed in Polysar Limited's Canadian Patents 1,017,492 and 1,030,699 relating to high green strength rubber. In the latex field the use of multi-valent ions, amines and diamines to coagulate

and/or cross link latex has also been disclosed.

U.S. Patent 2,754,280

discloses the formation of  
crosslinked films by coagulating dispersions of polymers  
5 containing acid or ester functional groups with a  
polyvalent metal ion. The coagulated films are "to all  
intents and purposes dispersions of crosslinked resins  
because pairs of carboxyl groups in various molecular  
chains are joined together, i.e. are crosslinked by the  
10 atoms of the polyvalent metals "(col. 1 lines 57 to 61)".  
A similar process is disclosed in U.S. Patent 2,959,821.

Processes for preparing latex useful as a binder in  
carpet backing applications are known in which a  
carboxylated latex is neutralized with ammonium  
15 hydroxide. Such latices are cured in the absence of heavy  
metal ions. These types of processes are disclosed in  
Canadian patent 808,713 and East German patent 137,593.

It is also known to impregnate webs with a latex of a  
functional polymer and to expose the impregnated web to  
20 amine vapour. The amine produces an in situ "thickening"  
of the latex.

The above art all teaches away from the use of  
monovalent ions as crosslinking agents. The conventional  
theory of ionic crosslinking requires a divalent metal  
25 compound or an ammonium complex. Thus, the use of a  
monovalent ion to cross link a functional polymer goes  
against the current state of the art.

British Patent Specification 1,085,833  
discloses an adhesive for

corrugated paper board comprising a carboxylated latex, a proteinaceous or carbohydrate binder and a crosslinking agent. The preferred crosslinking agents are urea formaldehyde or melamine formaldehyde resins. Complexes of polyvalent metal ions are also suitable as crosslinking agents. This art teaches away from the present case in that it does not suggest the use of a monovalent metal ion as a crosslinking agent. Furthermore there is no teaching that the carboxylated latex should be neutralized with a fixed alkali.

U.S. Patent 3,677,991 discloses a method of gelling a latex high in acrylate and containing from about 1.5 to 8 percent of a carboxylic acid monomer. The latex is irreversibly coagulated with a strong base, preferably ammonium hydroxide, but sodium hydroxide, potassium hydroxide and ethylene diamine are also suitable. The patent teaches that surfactant coverage on the latex particles is less than 100%. Coagulation does not take place until the pH is from 8.8 to 10.1. The patent does not teach that the gelled latex is useful as an adhesive.

Japanese Kokai 76/38,321 discloses a latex of a polymer containing from 20 to 80% of unsaturated carboxylic acid, 5 to 50% of butadiene and 0 to 75% of other comonomers. The latex when neutralized with ammonium hydroxide to a pH of 9 is useful as an adhesive for tiles.

Japanese Kokai 83/31,972 discloses a composition for use as a release coating. The composition is a latex of a copolymer of a C<sub>4-10</sub> alkylacrylate, and ethylenically unsaturated carboxylic acid, and a vinyl compound (ethylene dimethacrylate) which has been treated

with 0.2 to 1 equivalents of sodium acetate per equivalent of carboxylic acid. The document teaches that sodium ions provide better release properties than those obtained with calcium ions. The polymer of the Japanese Kokai contains  
5 ethylene dimethacrylate, a crosslinking agent, rather than the C<sub>2-4</sub> mono-olefin as required in the present invention.

British Patent 848,868

teaches a binder for non-woven webs. The binder comprises  
10 60 to 75% of one or more dienes of from 4 to 10 atoms, from 1 to 30% of a vinyl compound and from 1 to 39% of a monocarboxylic acid. Following polymerization the latex may be neutralized with ammonium hydroxide, an organic base or sodium hydroxide. The patent does not disclose  
15 any preference for neutralization with sodium hydroxide. Furthermore, the patent does not teach that such latices are useful as adhesives.

The present invention provides e.g. a latex characterised by comprising a latex of a polymer having a Tg  
20 less than about 0°C, formed by emulsion polymerizing a monomeric mixture selected from:

- (a) (i) from about 60-99.5 weight % of a C<sub>1-8</sub> alkyl or alkanol ester of acrylic or methacrylic acid; or a mixture thereof and  
25 (ii) from 0.5 to about 40 weight % of a C<sub>3-9</sub> ethylenically unsaturated acid; and  
(iii) from 0 up to about 5 weight % of an amide  
30 of a C<sub>3-9</sub> ethylenically unsaturated acid which amide may be unsubstituted or substituted at the nitrogen atom by a C<sub>1-8</sub> alkyl or alkanol radical; a C<sub>3-9</sub> ethylenically unsaturated aldehyde; or an

anhydride of a  $C_{4-8}$  ethylenically unsaturated dicarboxylic acid; or a mixture thereof;

- 5 (b) (i) from 0 to about 60 weight % of a vinyl aromatic monomer which may be unsubstituted or substituted by a  $C_{1-4}$  alkyl radical or a chlorine or bromine atom;
- 10 (ii) from 40 to 99 weight % of a mixture comprising 100 to 50 weight % of a  $C_{4-8}$  conjugated diolefin and 0 to 50 weight % of a  $C_{1-8}$  alkyl or alkanol, or a  $C_{2-8}$  alkenyl or alkenol ester of a  $C_{3-9}$  ethylenically unsaturated acid;
- 15 (iii) from about 0.5 to 10 weight % of a  $C_{3-9}$  ethylenically unsaturated acid; and
- 20 (iv) from 0 up to about 5 weight % of an amide of a  $C_{3-9}$  ethylenically unsaturated acid which amide may be unsubstituted or substituted at the nitrogen atom by a  $C_{1-8}$  alkyl or alkanol radical; a  $C_{3-9}$  ethylenically unsaturated aldehyde; or an anhydride of a  $C_{4-8}$  ethylenically unsaturated dicarboxylic acid; or a mixture thereof, and
- 25 (c) (i) up to about 40 weight % of a  $C_{2-4}$  mono-olefin unsaturated monomer;
- 30 (ii) from about 60 to 99.5 weight % of a  $C_{1-8}$  alkyl or alkanol ester of a  $C_{3-12}$  ethylenically unsaturated carboxylic acid or a  $C_{2-8}$  alkenyl or alkenol ester of a  $C_{1-12}$  saturated carboxylic acid or a mixture thereof; and
- (iii) from about 0.5 to 10 weight % of a  $C_{3-9}$  ethylenically unsaturated acid; and



- (iv) from 0 up to about 5 weight % of an amide of a  $C_{3-9}$  ethylenically unsaturated acid which amide may be unsubstituted or substituted at the nitrogen atom by a  $C_{1-8}$  alkyl or alkanol radical; a  $C_{3-9}$  ethylenically unsaturated aldehyde; or an anhydride of a  $C_{4-8}$  ethylenically unsaturated dicarboxylic acid; or a mixture thereof;
- wherein the adhesive has been adjusted to a pH of equal to or greater than about 6 with an agent selected from hydroxides and salts of lithium, sodium, potassium and a mixture thereof.
- Latexes used in accordance with the present invention may be classified as acrylic latices, carboxylated styrene-butadiene latexes optionally containing an acrylate or methacrylate ester, and functional vinyl ester latexes.
- The acrylic latices generally comprise a polymer of from about 0.5 to 40 weight %, usually from about 5 to 15 weight % of an acid monomer e.g. acrylic or methacrylic acid and up to about 10 weight % of another  $C_{3-8}$  ethylenically unsaturated acid, or a mixture thereof, or optionally a derivative of such acids, and the balance an ester of acrylic or methacrylic acid.
- The acid is usually a  $C_{3-9}$  ethylenically unsaturated carboxylic acid. Some co-polymerizable acids are acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid, butenoic acid, pentenoic acid, allylacetic acid, mesaconic acid, citraconic acid, hexenoic acid, muconic acid, heptenoic acid, octenoic acid, nonenoic acid, fumaric acid, itaconic acid, maleic acid, cinnamic acid, p-vinylbenzoic acid, and a mixture thereof.

In place of, or in conjunction with the acid the polymer may contain acid derivatives e.g. an amide of a  $C_{3-9}$  ethylenically unsubstituted acid. The amide may be unsubstituted or substituted at the nitrogen atom by a

5  $C_{1-8}$  alkyl or alkanol radical. Some amides are acrylamide, methacrylamide,  $\alpha$ -isopropylacrylamide, cinnamamide and the amides of unsaturated acids butenoic acid, pentenoic acid, hexenoic acid, heptenoic acid, and octenoic acid. Depending on the chain length

10 the unsaturation in the acid may occur between the 1 to 2 positions through the 8-9 positions. The amide radical may be substituted by alkyl or alkanol radicals containing up to 8 carbon atoms. The above amides represent the simplest homologues in the amide series up to octyl

15 amides, or hydroxooctyl amides. The lower amides are more commercially available e.g. acrylamide, methacrylamide, and  $C_{1-4}$  lower alkyl and alkanol derivatives thereof e.g. N-methylol acrylamide.

In place of, or in combination with either of the

20 ethylenically unsaturated acids or amides discussed above the copolymer may contain up to 10 weight %, preferably up to about 5 weight % of a  $C_{3-9}$  ethylenically unsaturated aldehyde. Some aldehydes are acrolein, methacrolein, butenaldehyde, pentenaldehyde,

25 hexenaldehyde, heptenaldehyde, octenaldehyde, and nonenaldehyde. As noted above the position of the double bond may vary along the carbon backbone of the monomer. Some additional aldehydes are cyclic aldehydes e.g. cinnamaldehyde.

30 The functional group in the acrylate polymer may be introduced by polymerizing an anhydride of a  $C_{4-9}$  ethylenically unsaturated dicarboxylic acid. Some anhydrides are maleic anhydride and phthalic anhydride.

The acrylic polymer also contains from about 60-90 weight %, preferably from about 60 to 75 weight % of a  $C_{1-8}$  alkyl or alkanol ester of acrylic or methacrylic acid. Some esters are methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, propyl acrylate, propyl methacrylate, butyl acrylate, butyl methacrylate, pentyl acrylate, pentyl methacrylate, hexyl acrylate, hexyl methacrylate, ethyl hexyl acrylate, ethyl hexyl methacrylate, heptyl acrylate, heptyl methacrylate, octyl acrylate, and octyl methacrylate. These monomers apart from hydroxy ethyl acrylate and hydroxy ethyl methacrylate may be substituted in the alkyl chain by a hydroxyl radical.

The styrene-butadiene type latices contain a polymer comprising up to about 60 weight % of a vinyl aromatic monomer, from about 40 to 99.5 weight % of a conjugated diolefin from about 0.5 to 10 weight % preferably not more than about 5 weight % of a functional monomer which is an ethylenically unsaturated acid, an amide of an ethylenically unsaturated acid, an ethylenically unsaturated aldehyde or an anhydride of an ethylenically unsaturated dicarboxylic acid. Optionally, up to about 50 weight per cent of the butadiene may be replaced with a  $C_{1-8}$  alkyl or alkanol or a  $C_{2-8}$  alkenyl or alkenol ester of a  $C_{3-9}$  ethylenically unsaturated acid, e.g. those discussed above in regard to the acrylate polymers.

Preferably the vinyl aromatic monomer is present in an amount from about 15 to 50 weight % of the polymer. Desirably the vinyl aromatic monomer is present in an amount from about 20 to 30 weight %. The vinyl aromatic polymer is preferably selected from styrene which is unsubstituted or substituted by a  $C_{1-4}$  alkyl radical or a chlorine or bromine atom. Some vinyl aromatic

monomers are a-methyl styrene, p-methyl styrene, chlorostyrene and bromostyrene. Other vinyl aromatic monomers may be used in place of styrene.

The conjugated diolefin should contain from 4 to 9  
5 carbon atoms. Preferably the conjugated diolefin is present in an amount from about 50 to 85 weight % of the polymer. Desirably the conjugated diolefin is present in an amount from about 70 to 80 weight %, most preferably about 75 weight %. The most commercially available  
10 conjugated diolefins are butadiene and isoprene.

The functional monomer may be an ethylenically unsubstituted acid, amide, aldehyde, or anhydride of a dicarboxylic acid. Some monomers have been discussed above with regard to the acrylate latexes. Preferably the  
15 functional monomer is used in amounts no greater than about 5 weight % of the polymer. It is most preferable if the total functional monomer is in the range from about 1 to 3.5 weight % of the total polymer. Mixtures of functional monomers are useful in accordance with the  
20 present invention. The most common combinations are unsaturated acid and unsaturated amide, and unsaturated acid and unsaturated aldehyde. For example the functional monomer may comprise about 2% amide and about 1.5% of carboxylic acid.

25 The functional vinyl ester latexes comprise up to about 40 weight % of a  $C_{2-4}$  mono-olefin monomer; from about 60% to about 99.5 weight % of a  $C_{1-8}$  alkanol ester of a  $C_{3-12}$  ethylenically unsaturated carboxylic acid or  $C_{2-8}$  alkenyl or alkenol ester of a  $C_{1-12}$  saturated  
30 carboxylic acid and from about 0.5 to 10 weight % of a functional monomer as described above. Preferably the mono-olefin monomer is present in an amount from about 1 to 25 weight %, most preferably from about 10 to 15 weight %. Some mono-olefins are ethylene, propylene and

butylene, with ethylene being preferred.

The ester component in the polymer may be a C<sub>1-8</sub> alkyl or alkanol ester of a C<sub>3-12</sub> ethylenically unsaturated acid or a C<sub>2-8</sub> alkenyl or alkenol ester of a C<sub>1-12</sub> saturated carboxylic acid. Some C<sub>3-12</sub> unsaturated carboxylic acids are acrylic acid, methacrylic acid, crotonic acid, pentenoic acid, hextenoic acid, heptenoic acid, octenoic acid and their homologues. Some alcohols which may be reacted with the unsaturated acids are saturated mono and diols of from 2 to 8 carbon atoms e.g. ethanol, propanol, butanol, pentanol, hexanol, ethyl hexanol, heptanol, octanol, and diol homologues of the foregoing alcohols.

The esters may also be the reaction product of a C<sub>2-8</sub> unsaturated alcohol or diol and a C<sub>1-12</sub> saturated carboxylic acid. Some alcohols are the C<sub>2-8</sub> alkenols and alkendiols e.g. propenol, butenol, pentenol, hexenol, heptenol and octenol and their diol homologues. Some acids are formic acid, acetic acid, propionic, butanoic, valeric, caproic, heptanoic and octenoic acids.

The most common of the foregoing esters are vinyl acetate, vinyl propionate, vinyl butanoate, and acrylate or methacrylate esters.

The functional monomer has been discussed above. It is preferably present in amounts not greater than about 5 weight %, most preferably from about 1-3 weight % of the total polymer consists of one or more functional monomers.

The molecular weight distribution of the polymer in the latex may be selected to provide improved tack. The selection of the molecular weight distribution of the SBR polymer is disclosed in applicants copending Canadian Patent Application S.N. 376,453 filed April 28, 1981. In addition to the teaching in the aforesaid Canadian Patent

application, it is desirable to use an SBR polymer having a molecular weight distribution so that up to about 90 weight % of the polymer has a molecular weight greater than about 320,000. Most preferably from about 25 to 55% of the polymer has a molecular weight greater than 320,000. The molecular weight distribution for a polymer in a latex may be determined by mixing the latex with a water compatible solvent for the polymer such as tetrahydrofuran. The insoluble polymer or gel will not dissolve in the solvent. A portion of the solvent and dissolved polymer is then passed through a gel permeation chromatograph column (GPC) to separate the polymer into fractions by molecular weight. The sum of the insoluble or gel content as a per cent of the total polymer in the latex plus the per cent of polymer with a molecular weight greater than 320,000 as determined by GPC will give the total per cent of polymer having a molecular weight greater than 320,000.

The latices of the present invention may be manufactured using conventional emulsion polymerization processes. An emulsion of the monomers in water is prepared. The emulsion may be stabilized with a surfactant which may be anionic, nonionic, or a mixture of anionic and nonionic surfactants. Some anionic surfactants are alkali, metal and alkaline earth metal salts of alkyl ether sulfates, alkyl phosphates, alkyl aryl phosphates, alkyl sulfonates, alkyl aryl sulfonates, and the like. Commercially available surfactants are listed in "McCutcheon's Emulsifiers and Detergents" published annually. In some latexes such as vinyl acetate, it may be desirable to incorporate a protective colloid e.g. polyvinyl alcohol or a naturally occurring thickener or a derivative thereof such as carboxymethyl cellulose. The polymerization may be catalyzed by a

redox-catalyst system or a free radical generating agent such as a peroxide. If desired a modifier such as t-dodecyl mercaptan or carbon tetrachloride may be employed. The reaction is short-stopped in a conventional manner. Up to this point all the procedures are conventional. Preferably, immediately following polymerization the latex is neutralized to a pH of at least about 6, e.g. about 6.5 to about 8.0, with a monovalent fixed alkali. The compounded latex may be neutralized with a monovalent fixed alkali to a pH of from about 6.5 to about 8.0 if monovalent fixed alkali, or a salt of a monovalent alkali, is added prior to any other base. Some bases are potassium hydroxide, sodium hydroxide or lithium hydroxide. The smaller the ion size of the alkali the greater the improvement in shear. The most practical base is sodium hydroxide. If desired the pH of the latex may be subsequently raised up to 14, preferably from about 8 to about 10 either using a monovalent fixed alkali base or any other type of base such as ammonia, or an amine. It is believed that the use of a fugitive base such as ammonium hydroxide in raising the pH from at least about 6 to about 8 to about 10 improves the hydrophobic properties of the adhesive.

Improved results are expected if the ingredients are selected to avoid chemicals which will generate ammonia or ammonium hydroxide during polymerization. Thus, it is advantageous to avoid the use of ammonium persulfate as a catalyst component and to avoid surfactants which will generate ammonia or ammonium hydroxide.

The adhesive of the present invention may include a tackifier resin. The tackifier resin optionally may be present in amounts up to about 170 parts by weight per 100 parts by weight of polymer. Conventionally the tackifier resin is present in an amount from about 15 to about 100 parts

by weight per 100 parts by weight of polymer.

- The tackifier resin may be rosin or hydrogenated rosin, a synthetic hydrocarbon tackifier or an acrylate. Suitable rosin or hydrogenated rosin esters have a ring and ball softening temperature from about 25 to about 115°C. Preferred tackifiers have a softening temperature from about 50 to about 110°C. Useful hydrocarbon tackifiers may be manufactured from a C<sub>9</sub> aromatic monomer or a C<sub>5</sub> aliphatic monomer or a mixture thereof.
- 5 and ball softening temperature from about 25 to about 115°C. Preferred tackifiers have a softening temperature from about 50 to about 110°C. Useful hydrocarbon tackifiers may be manufactured from a C<sub>9</sub> aromatic monomer or a C<sub>5</sub> aliphatic monomer or a mixture thereof.
- 10 These monomers are derived from the so-called C<sub>9</sub> and C<sub>5</sub> cuts in the fractionation of crude oil, or similar material. The synthetic hydrocarbon tackifier should have a ring and ball softening temperature from about 10 to about 100°C. Acrylic tackifier resins are polymerized
- 15 from one or more monomers selected from the group comprising acrylic acid which is unsubstituted or substituted by a C<sub>1-4</sub> alkyl or alkoxyl radical, or C<sub>1-6</sub> alkyl or alkanol esters thereof.

- The adhesives of the present invention may be applied
- 20 to conventional substrates. The substrates may be non-woven cellulosic material for use as price labels, or product labels. The substrates may be polymeric material such as a polyolefin. This type of substrate is used to manufacture adhesive tapes.

- 25 The substrate is usually relatively thin material, usually no greater than about 1/8 in (about 0.32 cm). The present invention contemplates that the adhesives could be used on other types of substrates. In the manufacture of tapes and labels the substrate is a
- 30 relatively thin sheet material. The sheet material may be a polymeric material which is flexible at about room temperature. The sheet material may be a homopolymer of an ethylenically unsaturated monomer such as ethylene, propylene or vinyl chloride, provided the substrate has



sufficient flexibility for the desired end use. The substrate may also be a copolymer containing an ethylenically unsaturated monomer such as ethylene, propylene, vinyl chloride, and one or more copolymers  
5 selected from unsaturated mono- or di-carboxylic acid monomers such as maleic acid, fumaric acid, acrylic acid, methacrylic acid, adipic, propenoic, butenoic, and pentenoic acids, an ester monomer, such as  $C_9-C_{15}$   
10 esters of such acids, or an amide monomer having about 4 - 10 carbon atoms. Thus, the sheet material may be polyester or a polyamide. The substrate may be made from cellulosic or reconstituted cellulosic material such as rayon. The substrate need not be a sheet material but may be composed of fibers which may be woven, or non woven as  
15 is the case in paper. The woven substrate may be made from cellulosic material, such as cotton or from fibers of any of the above-mentioned polymers.

The composition is applied to the substrate using conventional coating techniques such as roller coaters,  
20 blade coaters, meyer rods or air coaters. The coated substrate is then dried usually by passing it through a heating tunnel or oven which may use circulating hot air or infrared lamps to dry the coated substrate. The drying time will be a function of a number of factors such as the  
25 heat capacity of the substrate, the type of heating, the oven temperature, air velocities (if circulating air is used) and the rate of passage of the substrate through the oven or heating tunnel. The manufacturer may readily determine suitable time/temperature relationships to  
30 determine optimum drying conditions in his equipment for the product.

The substrate should be coated with sufficient adhesive to provide a dry coat weight from about 10 to about 35 pounds per 3,000 per  $ft^2$  ( about 4.5 to about  
35 15.9 Kg per 278.7  $m^2$ ). Generally, in the

manufacture of tapes using a continuous sheet polymeric substrate dry coat weight of about 17 to about 18 pounds per 3,000 ft<sup>2</sup> ( about 7.7 to about 8.2 Kg per 278.7 m<sup>2</sup>) are used. In the manufacture of labels a dry coating weight of about 12 to about 18 pounds per 3,300 ft<sup>2</sup> ( about 5.4 to about 8.2 Kg per 306.6 m<sup>2</sup>) is usually used. In the manufacture of masking tape, a dry coating weight of about 25 to about 35 pounds per 3,000 ft<sup>2</sup> ( about 11.3 to about 15.9 Kg per 278.7 m<sup>2</sup>) is usually used.

After drying, the coated substrate is cut to the required dimension. In the manufacture of tape the substrate is cut into strips and rolled to provide a finished product. The substrate may also be cut into shaped items to provide labels or medicinal tapes. These processes are known to those in the tape industry.

The following non-limiting examples illustrate the present invention.

A styrene butadiene carboxylic latex was prepared using conventional emulsion polymerization techniques. The monomeric mixture comprised about 25 weight % styrene, about 2 weight % itaconic acid, and balance butadiene. The latex was stripped of residual monomers and then subjected to different treatments. A sample of latex was untreated. A sample of latex was neutralized with ammonium hydroxide to pH's of 7.0, 8.5, 10.0. A sample of latex was neutralized to pH's of 7.0, 8.5, 10.1 with sodium hydroxide. Samples of the latices were then blended with 30 parts by weight of a hydrogenated ester ( Stabelite Ester 10 - trademark) per 100 parts by weight of polymer. The samples were then applied to a Mylar ( trademark) film at a coat weight of about 23 g/m<sup>2</sup> and a thickness of about 0.003 cm ( about 1 mil). The coating was dried and the resulting tape subjected to a standard shear (PSTC) test using 1 Kg weight. The time until the weight and tape fell off the plate was recorded. Table I shows the results.

TABLE I

Latex	Time to Shear Failure (hours)
Control	0.8
Control + $\text{NH}_4\text{OH}$ (pH 7)	9.9
Control + $\text{NH}_4\text{OH}$ (pH 8)	9.0
Control + $\text{NH}_4\text{OH}$ (pH 10)	15.5
Control + $\text{NaOH}$ (pH 7)	70.0
Control + $\text{NaOH}$ (pH 8)	70.0
Control + $\text{NaOH}$ (pH 10.1)	70.0
Control + tackifier	0.1
Control + $\text{NH}_4\text{OH}$ (pH 7) + tackifier	0.1
Control + $\text{NH}_4\text{OH}$ (pH 8) + tackifier	0.2
Control + $\text{NH}_4\text{OH}$ (pH 10) + tackifier	0.2
Control + $\text{NaOH}$ (pH 7) + tackifier	1.9
Control + $\text{NaOH}$ (pH 8) + tackifier	2.7
Control + $\text{NaOH}$ (pH 10.1) + tackifier	1.9

The tack of the adhesives was compared using a rolling ball test. The tack of the samples at pH of 8 or less was substantially similar. In the samples at pH greater than 10 there was some decrease in the tack of the adhesive.

To illustrate the present invention a water based acrylate adhesive was prepared in accordance with Run #2 of Example 1 of United States Patent 4,316,830. Following polymerization and the addition of t-butyl perbenzoate and the sodium formaldehyde sulfoxylate, the latex was divided into three samples. One sample had a pH of about 3.9 and was not neutralized. One sample was neutralized to a pH of 8.5 with sodium hydroxide and one sample was neutralized to a pH of 8.5 with ammonium hydroxide. Sample tapes were made and tested in accordance with the procedures described in the 830 patent. The results are set forth in Table II.

TABLE II

<u>Latex</u>	<u>Shear (1/2"x1"x1 kg)</u> <u>hours</u>	<u>180° peel</u> <u>5 min. (lb/in)</u>
not neutralized	Mean 3.1	2.04 (0.36Kg/cm)
pH 8.5 NH <sub>4</sub> OH	" 3.6	1.78 (0.32Kg/cm)
pH 8.5 NaOH	" 73.8	1.67 (0.30Kg/cm)

The neutralization of the acrylate latex with sodium hydroxide resulted in about a 30-fold increase in the time to shear failure relative to the unneutralized sample, and the sample neutralized with ammonium hydroxide. Neutralization with sodium hydroxide marginally reduced the 180° peel but not sufficiently to cause serious concern.

It will be appreciated that the present invention includes providing aqueous based adhesives having improved shear properties, the adhesives being prepared from acrylate type latices, styrene-butadiene type latices, or ethylene-vinyl acetate type latices, which contain a carboxylic acid monomer, and have been neutralized to a pH of e.g. about 6.5 to about 8.0, following polymerization with an alkali metal base.

Claims

1. An adhesive, characterised by comprising a latex of a polymer having a  $T_g$  less than about  $0^{\circ}\text{C}$ , formed by emulsion polymerizing a monomeric mixture selected from:
- 5 (a)(i) about 60.0 to about 99.5 weight % of a  $\text{C}_{1-8}$  alkyl or alkanol ester of acrylic or methacrylic acid; or a mixture thereof;
- (ii) about 0.5 to about 40.0 weight % of a  $\text{C}_{3-9}$  ethylenically unsaturated carboxylic acid;
- 10 (iii) from 0 to about 5 weight % of an amide of a  $\text{C}_{3-9}$  ethylenically unsaturated carboxylic acid, which amide may be unsubstituted or substituted at the nitrogen atom by a  $\text{C}_{1-8}$  alkyl or alkanol radical; a  $\text{C}_{3-9}$  ethylenically unsaturated aldehyde; or an
- 15 anhydride of a  $\text{C}_{4-8}$  ethylenically unsaturated dicarboxylic dicarboxylic acid; or a mixture thereof;
- (b)(i) 0 to about 60 weight % of a vinyl aromatic monomer, which may be unsubstituted or substituted by a  $\text{C}_{1-4}$  alkyl radical or a chlorine or bromine atom;
- 20 (ii) about 40 to about 99 weight % of a mixture comprising about 100 to about 50 weight % of a  $\text{C}_{4-8}$  conjugated diolefin and 0 to about 50 weight % of a  $\text{C}_{1-8}$  alkyl or alkanol, or a  $\text{C}_{2-8}$  alkenyl or alkenol ester of a  $\text{C}_{3-9}$  ethylenically unsaturated carboxylic
- 25 acid;
- (iii) about 0.5 to about 10.0 weight % of a  $\text{C}_{3-9}$  ethylenically unsaturated carboxylic acid;
- (iv) 0 to about 5 weight % of an amide of a  $\text{C}_{3-9}$  ethylenically unsaturated carboxylic acid, which amide
- 30 may be unsubstituted or substituted at the nitrogen atom by a  $\text{C}_{1-8}$  alkyl or alkanol radical; a  $\text{C}_{3-9}$  ethylenically unsaturated aldehyde; or an anhydride of a  $\text{C}_{4-8}$  ethylenically unsaturated dicarboxylic acid; or a mixture thereof;

- (c)(i) up to about 1 to about 40 weight % of a  $C_{2-4}$  mono-olefin monomer;
- (ii) about 60.0 to about 99.5 weight % of a  $C_{1-8}$  alkyl or alkanol ester of a  $C_{3-12}$  ethylenically unsaturated carboxylic acid or a  $C_{2-8}$  alkenyl or alkenol ester of a  $C_{1-12}$  saturated carboxylic acid; or a mixture thereof;
- (iii) about 0.5 to about 10.0 weight % of a  $C_{3-9}$  ethylenically unsaturated carboxylic acid;
- 10 (iv) 0 to about 5 weight % of an amide of a  $C_{3-9}$  ethylenically unsaturated carboxylic acid, which amide may be unsubstituted or substituted at the nitrogen atom by a  $C_{1-8}$  alkyl or alkanol radical; a  $C_{3-9}$  ethylenically unsaturated aldehyde; or an
- 15 anhydride of a  $C_{4-8}$  ethylenically unsaturated dicarboxylic acid; or a mixture thereof;
- wherein said adhesive has been adjusted to a pH

greater than about 6, said adjustment comprising utilising an agent selected from hydroxides and salts of lithium, sodium, potassium, and a mixture thereof.

2. An adhesive as claimed in claim 1, characterised by said polymer has a molecular weight distribution so that about 20 to about 55 weight % of the polymer has a molecular weight greater than about 320,000.

3. An adhesive as claimed in claim 1 or 2, characterised by said monomeric mixture contains about 15 to about 50 weight % of a vinyl aromatic monomer selected from styrene, p-methyl styrene,  $\alpha$ -methyl styrene, chlorostyrene, and a mixture thereof; and from about 85 to about 50 weight % of a conjugated diolefin selected from butadiene, isoprene, and a mixture thereof.

4. An adhesive as claimed in claim 1 or 2, characterised by said monomeric mixture contains:  
(i) about 5 to about 15 weight % of acrylic acid, methacrylic acid, or a mixture thereof;  
(ii) about 60 to about 90 weight % of a  $C_{1-8}$  alkyl or alkanol ester of acrylic or methacrylic acid;  
(iii) 0 to about 10 weight % of a  $C_{3-9}$  ethylenically unsaturated carboxylic acid other than acrylic acid or methacrylic acid;  
(iv) 0 to about 5 weight % of an amide of a  $C_{3-8}$  ethylenically unsaturated carboxylic acid, which amide may be unsubstituted or substituted at the nitrogen atom by a  $C_{1-8}$  alkyl or alkanol radical; a  $C_{3-9}$  ethylenically unsaturated aldehyde; or an anhydride of a  $C_{4-8}$  ethylenically unsaturated dicarboxylic acid; or a mixture thereof.

5. An adhesive as claimed in claim 1 or 2, characterised by said monomeric mixture contains:  
(i) 0 to about 60 weight % of a vinyl aromatic monomer, which may be unsubstituted or substituted by

- a C<sub>1-4</sub> alkyl radical or a chlorine or bromine atom;  
(ii) about 40.0 to about 99.5 weight % of a C<sub>4-8</sub> conjugated diolefin;  
(iii) about 0.5 to about 10.0 weight % of a C<sub>3-9</sub> ethylenically unsaturated carboxylic acid;  
5 (iv) 0 to about 5 weight % of an amide of a C<sub>3-9</sub> ethylenically unsaturated carboxylic acid, which amide may be unsubstituted or substituted at the nitrogen atom by a C<sub>1-8</sub> alkyl or alkanol radical; a C<sub>3-9</sub>  
10 ethylenically unsaturated aldehyde; or an anhydride of a C<sub>4-8</sub> ethylenically unsaturated dicarboxylic acid; or a mixture thereof.
6. An adhesive as claimed in any one of claims 1 to 5, to 5, characterised by said monomeric mixture  
15 contains acid selected from acrylic acid, methacrylic acid, fumaric acid, itaconic acid, maleic acid, cinnamic acid, and a mixture thereof.
7. An adhesive as claimed in any one of claims 1 to to 6, characterised by said monomeric mixture  
20 contains amide selected from acrylamide, methacrylamide, N-methylolacrylamide, and a mixture thereof.
8. An adhesive as claimed in claim 7, characterised by said amide is present up to about 3 weight %.
- 25 9. An adhesive as claimed in any one of claims 1 to 8, characterised by comprising a tackifier in an amount about 15 to about 100 parts by weight per 100 parts by weight of polymer, said tackifier being selected from:
- 30 (a) rosin or a hydrogenated rosin ester which has a ring and ball softening temperature from about 25 to about 115°C;  
(b) a synthetic hydrocarbon tackifier resin having a ring and ball softening temperature from about 10 to  
35 about 100°C, manufactured from a C<sub>9</sub> aromatic monomer,



or a mixture of tackifiers manufactured from a C<sub>9</sub> aromatic monomer, and a C<sub>5</sub> aliphatic monomer;

(c) an acrylic resin selected from polymers of one or more of acrylic acid which is unsubstituted or  
5 substituted by a C<sub>1-4</sub> alkyl or alkoxy radical, or C<sub>1-6</sub> alkyl esters thereof.

10. A sheet substrated, characterised by said sheet substrate is coated with an adhesive composition as claimed in any one of claims 1 to 9.

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